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HABITABLE ATMOSPHERES WHICH DO NOT SUPPORT COMBUSTION

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ABSTRACT

A concept has emerged in our laboratories which promises to represent a major advance in fire protection systems for confined spaces. It appears that habitable atmospheres can be developed in which humans will be able to live and function normally for extended periods of time with no physiological harm, but which at the same time will not support combustion of ordinary materials such as paper, cloth, gasoline, etc. These atmospheres might contain 3 psia partial pressure of oxygen as does ordinary air; or oxygen-enriched atmospheres as used in aerospace environments could be employed. In addition, certain inert polyatomic gases, namely, CF_4, C_2F_6 or C_3F_8, are incorporated into the atmosphere. These impart the property of completely suppressing flammability, while retaining the life support capability. These perfluorinated agents are not to be confused with other halogenated compounds that contain elements other than carbon and fluorine in the molecule. Some of the other compounds, notably CF_3Br (Halon 1301), are effective fire suppressants but are not physciologically inert.

At the present time a major program is being conducted under sponsorship of the U. S. Army, Office of the Chief of Research and Development (Contract DAHC19-71-C0026) to evaluate the validity of the concept. The program involves measurement of materials flammability in the atmospheres, determination of the stability of the atmospheres under fire conditions, and an animal toxicology study which will include cardiac sensitization tests. Program results to date, while favorable, are too incomplete to form the basis of a conclusive report. The study will be completed in March, 1972, and at that time a full manuscript will be prepared for distribution at the Sixth IES/AIAA/ASTM Space Simulation Conference in May. In the following discussion of the present abstract, a summary of the background of the concept is presented, together with some technical data from various laboratories, and an outline of the research investigation that is being conducted.

As a result of applied research programs that were carried out at Atlantic Research and elsewhere, (1-3) it became known that the rate of flame spread over burning material was a strong inverse function of the heat capacity per mole of oxygen of the

oxidizing atmosphere. Thus, for example, cotton fabric burns in a 21/79, O_2/He atmosphere (C_p=27 cal/°C mole O_2) at roughly three times the rate it burns in air (C_p=33 cal/°C mole O_2). It was discovered that if the heat capacity of the atmosphere could be raised to ~50 cal/°C mole O_2, the atmospheres would not support combustion of any ordinary material. Many properties of the environment determine the rate of flame spread, and the simple correlation with heat capacity obtains because the agents being considered are inert and only act physically to suppress combustion; they exhibit no chemical inhibiting action as many flame suppressants do (4). Combustion depends on the feedback of energy from the flame zone to the unburned fuel in order to bring it to the combustion temperature. Inert gas diluents act as heat sinks for the combustion energy, cooling the flame and interfering with this feedback process and, at sufficiently high concentrations, quenching combustion.

However, the atmosphere plays a different role in sustaining life than in supporting combustion. The life support function requires a partial pressure (~2.5 psi or greater) of oxygen sufficient to maintain the necessary oxygen tension in the blood. Diluent gases, if they are physiologically inert, have only a minor effect on this process. Hence, by the selection of a proper additive it should be possible to prepare an atmosphere of high heat capacity that is also physciologically inert. This would comprise a habitable atmosphere that would not support combustion.

After a literature search and an in-house experimental program, it was found that the completely-fluorinated lower hydrocarbons comprised a class of compounds which apparently fulfilled all the requirements of the concept. At present the candidate agents which appear most promising are CF_4, C_2F_6 and C_3F_8. The amounts of these materials that must be added to air to completely suppress the ignition and flame propagation of four selected materials were found to be:

Material	Volume % Fluorocarbon Added to Air	Heat Capacity (cal/°C mole O_2)
Cotton Flannel	18.7% CF_4	49
	11.0% C_2F_6	48
	9.4% C_3F_8	51
Tissue Paper	12.0% C_2F_6	49
Foam Plastic	3.1% C_2F_6	37
Kerosine	7.3% C_2F_6	43

Listed in the last column of the above table are the heat capacities of the air/fluorocarbon atmospheres. The addition of agent to air, of course, reduces the O_2 concentration, but even

in the worst case above (18.7%) the O_2 content is 17.0%. This corresponds to the O_2 partial pressure that is present at an altitude of approximately 5000 feet; hence, no serious physiological effect will occur.

Materials have also been found to be non-flammable in oxygen-enriched atmospheres containing > 40% O_2 provided sufficient fluorocarbon is present. In the current testing program, the flammability of numerous materials including cellulosics, plastics, solvents, etc., will be measured for a range of fluorocarbon/air mixtures.

The effectiveness of the agents as fire suppressants is well established by the experimental program of which the above examples represent a sampling of the results. It is equally important to determine whether these agents are physiologically inert. This latter aspect of the concept could not be settled as conclusively as the combustion aspect because of the paucity of toxicological data on these agents. However, the results of the limited studies that have been conducted are entirely favorable and indicate a complete lack of physiological activity for these compounds. Before citing specific examples of the physiological inertness of the agents, it should be mentioned again that the completely fluorinated compounds being discussed here are not to be classed with other Halons which contain elements other than fluorine in the molecules (Br, Cl, H). Other halocarbons do exhibit pharmacological or neurological effects and would not be suitable for use as habitable atmospheres.

The most extensive toxicological study involving any compounds of the perfluorocarbon class is that of Clayton et al. on octafluorocyclobutane (5). Mice, rats, rabbits and dogs were exposed to a 10% concentration of the fluorocarbon in air six hours a day for a total of 90 exposures. Detailed studies during and after the exposure program showed no observable physiological effects. As a result of these studies, octaflurorcyclobutane has received FDA approval for use in food aerosols.

Toxicity data on the straight chain fluorocarbons are much more limited. However, because of their much greater stability, they might be expected to be even more inactive than the cyclic compound. Clayton (6) reports single four hour exposures of mice or rats to atmospheres containing 80% CF_4, C_2F_6, or C_4F_{10} and 20% oxygen without evidence of anesthetic effects or physiological damage. There is thus substantial reason to believe that mammals, and presumably humans, could live for extended periods of time in atmospheres containing certain fully saturated fluorocarbons in concentrations sufficient to suppress combustion without impairment of faculties or permanent harm. Much more data must be accumulated, however, including human exposure data, before the safety and effectiveness of this approach to fire safety can be fully assessed.

The present program is designed to develop these necessary toxicology data in animal studies, but will not include human exposures at present. Three types of animal studies are underway: 1) acute inhalation; 2) ten-day inhalation; and 3) cardiac sensitization. In the first of these, LC_{50} levels (if any) for male rats will be measured for the three candidate fluorocarbons. In the second study, continuous exposure of rats and guinea pigs for 10 days will be conducted at the usage concentration of the agents. The animals will be subjected to clinical observations, hematological and biochemical studies. Following terminal sacrifice, gross pathologic and histopathologic examinations will be performed. The cardiac sensitization studies will involve subjecting dogs to the usage concentrations of the agents. EKG patterns will be monitored with and without exogenously delivered epinephrine.

It is envisioned that the habitable atmospheres will be employed in two types of modes. The first type will be as a continuously present atmosphere which will prevent combustion from initiating. In the second mode, the agents will be dispersed into a confined chamber to extinguish a fire after it starts. Occupants of the chamber would then not have to evacuate afterwards. The second mode of application requires that the stability of the agents to fire conditions be known, and also that the toxicity of any decomposition products be determined. Scaled fire tests are being conducted to investigate both of these problems. Chemical analyses of decomposition products are being made for a range of conditions, and animal exposures to the pre- and post-fire atmospheres are planned. Complete post-exposure examinations of the animals as described for the 10-day inhalation study will be made.

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